

We Claim:

1. A multiphoton-activatable, photoreactive composition comprising (a) at least one reactive species that is capable of undergoing an acid- or radical-initiated chemical reaction; (b) a photochemically-effective amount of a multiphoton photosensitizer comprising at least one multiphoton up-converting inorganic phosphor; and (c) a photochemically-effective amount of a one-photon photoinitiator system that is capable of being photosensitized by said multiphoton photosensitizer.

2. The composition of Claim 1 wherein said reactive species is a curable species.

3. The composition of Claim 2 wherein said curable species is selected from the group consisting of monomers, oligomers, reactive polymers, and mixtures thereof.

4. The composition of Claim 3 wherein said curable species is selected from the group consisting of addition-polymerizable monomers and oligomers, addition-crosslinkable polymers, cationically-polymerizable monomers and oligomers, cationically-crosslinkable polymers, and mixtures thereof.

5. The composition of Claim 1 wherein said reactive species is a non-curable species.

6. The composition of Claim 1 wherein said multiphoton up-converting inorganic phosphor comprises at least one host material that is doped with at least one rare earth activator couple.

7. The composition of Claim 6 wherein said host material is selected from the group consisting of metal oxysulfides, metal oxyhalides, metal fluorides, metal gallates, metal silicates, metal aluminates, metal phosphates, metal oxides, metal vanadates, and mixtures thereof.

8. The composition of Claim 6 wherein said rare earth activator couple comprises an absorber that is ytterbium and an emitting center that is selected from the group consisting of erbium, holmium, terbium, thulium, and mixtures thereof.

5 9. The composition of Claim 8 wherein the molar ratio of said absorber to said emitter is at least about 1:1.

10 10. The composition of Claim 1 wherein said multiphoton up-converting inorganic phosphor is capable of multiphoton absorption of long-wavelength visible or near-infrared radiation and single-photon emission of ultraviolet or visible radiation.

15 11. The composition of Claim 1 wherein said multiphoton up-converting inorganic phosphor is in the form of particles having an average diameter less than about 7 microns.

12. The composition of Claim 11 wherein said particles have been coated or treated with at least one surface-active, compatibilizing agent.

20 13. The composition of Claim 1 wherein said multiphoton up-converting inorganic phosphor is selected from the group consisting of those represented by the following formulas: $\text{Na}(\text{Y}_x\text{Yb}_y\text{Er}_z)\text{F}_4$, where x is 0.7 to 0.9, y is 0.09 to 0.29, and z is 0.05 to 0.01; $\text{Na}(\text{Y}_x\text{Yb}_y\text{Ho}_z)\text{F}_4$, where x is 0.7 to 0.9, y is 0.0995 to 0.2995, and z is 0.0005 to 0.001; $\text{Na}(\text{Y}_x\text{Yb}_y\text{Tm}_z)\text{F}_4$, where x is 0.7 to 0.9, y is 0.0995 to 0.2995, and z is 0.0005 to 0.001; $(\text{Y}_x\text{Yb}_y\text{Er}_z)\text{O}_2\text{S}$, where x is 0.7 to 0.9, y is 0.05 to 0.12, and z is 0.05 to 0.12; and $(\text{Y}_{0.86}\text{Yb}_{0.08}\text{Er}_{0.06})_2\text{O}_3$.

25 14. The composition of Claim 13 wherein said multiphoton up-converting inorganic phosphor is $(\text{Y}_{0.86}\text{Yb}_{0.08}\text{Er}_{0.06})\text{O}_2\text{S}$.

30 15. The composition of Claim 1 wherein said one-photon photoinitiator system comprises a photochemically effective amount of at least one one-photon photoinitiator

that has an electronic absorption band that overlaps with an up-converted electronic emission band of said multiphoton photosensitizer.

5 16. The composition of Claim 15 wherein said one-photon photoinitiator is selected from the group consisting of free-radical photoinitiators that generate a free radical source and cationic photoinitiators that generate an acid when exposed to ultraviolet or visible radiation.

10 17. The composition of Claim 16 wherein said free-radical photoinitiators are selected from the group consisting of acetophenones, benzophenones, aryl glyoxalates, acylphosphine oxides, benzoin ethers, benzil ketals, thioxanthenes, chloroalkyltriazines, bisimidazoles, triacylimidazoles, pyrylium compounds, sulfonium salts, iodonium salts, mercapto compounds, quinones, azo compounds, organic peroxides, and mixtures thereof; and said cationic photoinitiators are selected from the group consisting of metallocene salts having an onium cation and a halogen-containing complex anion of a metal or metalloid, metallocene salts having an organometallic complex cation and a halogen-containing complex anion of a metal or metalloid, iodonium salts, sulfonium salts, and mixtures thereof.

20 18. The composition of Claim 1 wherein said one-photon photoinitiator system comprises photochemically effective amounts of (1) at least one one-photon photosensitizer having an electronic absorption band that overlaps with an up-converted electronic emission band of said multiphoton photosensitizer; and (2) either or both of (i) at least one electron donor compound different from said one-photon photosensitizer and capable of donating an electron to an electronic excited state of said one-photon photosensitizer; and (ii) at least one photoinitiator that is capable of being photosensitized by accepting an electron from an electronic excited state of said one-photon photosensitizer, resulting in the formation of at least one free radical and/or acid.

30 19. The composition of Claim 18 wherein said composition comprises both said electron donor compound and said photoinitiator.

20. The composition of Claim 18 wherein said one-photon photosensitizer is capable of absorbing light within the range of wavelengths between about 300 and about 800 nanometers and is capable of sensitizing 2-methyl-4,6-bis(trichloromethyl)-s-triazine.

5 21. The composition of Claim 18 wherein said one-photon photosensitizer is selected from the group consisting of ketones, coumarin dyes, xanthene dyes, acridine dyes, thiazole dyes, thiazine dyes, oxazine dyes, azine dyes, aminoketone dyes, porphyrins, aromatic polycyclic hydrocarbons, p-substituted aminostyryl ketone
10 compounds, aminotriaryl methanes, merocyanines, squarylium dyes, pyridinium dyes, and mixtures thereof.

22. The composition of Claim 18 wherein said one-photon photosensitizer is selected from the group consisting of xanthene dyes, ketones, ketocoumarins,
15 aminoarylketones, p-substituted aminostyryl ketone compounds, and mixtures thereof.

23. The composition of Claim 18 wherein said one-photon photosensitizer is selected from the group consisting of rose bengal, camphorquinone, glyoxal, biacetyl,
20 3,3,6,6-tetramethylcyclohexanedione, 3,3,7,7-tetramethyl-1,2-cycloheptanedione, 3,3,8,8-tetramethyl-1,2-cyclooctanedione, 3,3,18,18-tetramethyl-1,2-cyclooctadecanedione, dipivaloyl, benzil, furil, hydroxybenzil, 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione, 3,4-hexanedione, 2,3-heptanedione, 3,4-heptanedione, 2,3-octanedione, 4,5-octanedione, 1,2-cyclohexanedione, and mixtures thereof.

25 24. The composition of Claim 18 wherein said electron donor compound has an oxidation potential that is greater than zero and less than or equal to that of p-dimethoxybenzene.

30 25. The composition of Claim 18 wherein said electron donor compound has an oxidation potential between about 0.3 and 1 volt vs. a standard saturated calomel electrode.

26. The composition of Claim 18 wherein said electron donor compound is selected from the group consisting of amines, amides, ethers, ureas, sulfinic acids and their salts, salts of ferrocyanide, ascorbic acid and its salts, dithiocarbamic acid and its salts, salts of xanthates, salts of ethylene diamine tetraacetic acid, salts of (alkyl)_n(aryl)_mborates (n + m = 4), SnR₄ compounds (where each R is independently chosen from the group consisting of alkyl, aralkyl, aryl, and alkaryl groups), ferrocene, and mixtures thereof.

27. The composition of Claim 26 wherein said electron donor compound is selected from the group consisting of amines that contain one or more julolidinyl moieties, alkylarylborate salts, salts of aromatic sulfinic acids, 4-dimethylaminobenzoic acid, ethyl 4-dimethylaminobenzoate, 3-dimethylaminobenzoic acid, 4-dimethylaminobenzoin, 4-dimethylaminobenzaldehyde, 4-dimethylaminobenzonitrile, 4-dimethylaminophenethyl alcohol, 1,2,4-trimethoxybenzene, and mixtures thereof.

28. The composition of Claim 18 wherein said composition contains no said electron donor compound.

29. The composition of Claim 18 wherein said photoinitiator is selected from the group consisting of iodonium salts, sulfonium salts, diazonium salts, azinium salts, chloromethylated triazines, triarylimidazolyl dimers, and mixtures thereof.

30. The composition of Claim 29 wherein said photoinitiator is selected from the group consisting of iodonium salts, chloromethylated triazines, triarylimidazolyl dimers, sulfonium salts, diazonium salts, and mixtures thereof.

31. The composition of Claim 30 wherein said photoinitiator is selected from the group consisting of arylodonium salts, chloromethylated triazines, 2,4,5-triphenylimidazolyl dimers, and mixtures thereof.

32. The composition of Claim 1 wherein said composition comprises from about 5% to about 99.79% by weight of said reactive species, from about 0.01% to about

10% by weight of said multiphoton photosensitizer, and from about 0.1% to about 15% by weight of said one-photon photoinitiator system.

5 33. The composition of Claim 1 wherein said composition further comprises at least one adjuvant selected from the group consisting of solvents, diluents, resins, binders, plasticizers, pigments, dyes, inorganic or organic reinforcing or extending fillers, thixotropic agents, indicators, inhibitors, stabilizers, ultraviolet absorbers, and medicaments.

10 34. A multiphoton-activatable, photoreactive composition comprises: (a) at least one curable species that is capable of undergoing a radical-initiated chemical reaction; (b) a photochemically-effective amount of a multiphoton photosensitizer comprising at least one multiphoton up-converting inorganic phosphor represented by the general formula $(Y_xY_bY_c)O_2S$, where x is 0.7 to 0.9, y is 0.05 to 0.12, and z is 0.05 to 0.12; and (c) photochemically effective amounts of (1) rose bengal; (2) at least one alkylarylborate salt; and (3) at least one iodonium salt.

15 35. A method of multiphoton photosensitizing comprising the steps of
20 (a) preparing a multiphoton-activatable, photoreactive composition comprising
(1) at least one reactive species that is capable of undergoing an acid- or radical-initiated chemical reaction;
(2) a photochemically-effective amount of a multiphoton photosensitizer comprising at least one multiphoton up-converting inorganic phosphor; and
25 (3) a photochemically-effective amount of a one-photon photoinitiator system that is capable of being photosensitized by said multiphoton photosensitizer; and

30 (b) irradiating said composition with light sufficient to cause sequential or simultaneous absorption of at least two photons, thereby inducing at least one acid- or radical-initiated chemical reaction where said composition is exposed to the light.

36. The method of Claim 35 wherein said irradiating is carried out using a continuous wave laser source.

37. The method of Claim 35 wherein said irradiating is carried out using a laser diode.

38. The method of Claim 35 wherein said irradiating is pulse irradiating.

39. The method of Claim 38 wherein said pulse irradiating is carried out using a near infrared pulsed laser having a pulse length less than about 10^{-8} second.

40. The method of Claim 35 wherein said method provides linear imaging speeds of about 5 to about 100,000 microns/second.

41. The method of Claim 35 wherein said absorption is sequential.